



3641

Confirmation Number 4911

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of VELTMANS

Application No.: 09/517,426

Filed: March 2, 2000

For: PROCESS FOR THE PREPARATION OF
CRYSTALLINE ENERGETIC MATERIALS

T/C - 3641

Examiner: Edward Miller

Attorney Docket No. 7389/80653

December 19, 2003

CLAIM OF PRIORITY PER RULE 55
AND 35 U.S.C. 119


Assistant Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

Applicant hereby requests that the above-identified application be treated as having the benefit of the foreign priority and entitled to all rights accorded by Title 35, U.S. Code, Section 119, based on EP 99200592.6, filed March 2, 1999, a certified copy of which is attached hereto.

Respectfully submitted,

FITCH, EVEN, TABIN & FLANNERY

By: 

Kendrew H. Colton
Registration No. 30,368

Fitch, Even, Tabin & Flannery
1801 K Street, N.W. - Suite 401L
Washington, D.C. 20006-1201
Telephone No. (202) 419-7000
Facsimile No. (202) 419-7007

#261 Priority Document
2-3-04

RECEIVED
DEC 23 2003
GROUP 3600

THIS PAGE BLANK (USPTO)



Eur päisches
Patentamt

Eur pean
Patent Office

Office eur péen
des brevets

Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

99200592.6

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.



C. v.d. Aa-Jansen

MÜNCHEN, DEN
MUNICH,
MUNICH, LE

25/11/03

THIS PAGE BLANK (USPTO)



Eur päisches
Patentamt

Eur pean
Patent Office

Office européen
des brevets

**Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation**

Anmeldung Nr.:
Application no.: 99200592.6
Demande n°:

Anmeldetag:
Date of filing: 02/03/99
Date de dépôt:

Anmelder:
Applicant(s):
Demandeur(s):

Nederlandse Organisatie voor toegepast-natuurwetenschappelijk onderzoek TNO
2628 VK Delft
NETHERLANDS

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:

Process for the production of crystalline energetic materials

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat:
State:
Pays:

Tag:
Date:
Date:

Aktenzeichen:
File no.
Numéro de dépôt:

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:

C06B21/00, C30B30/06, C30B7/00, B01J2/18

Am Anmeldetag benannte Vertragsstaaten:
Contracting states designated at date of filing:
Etats contractants désignés lors du dépôt:

AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE

Bemerkungen:
Remarks:
Remarques:

THIS PAGE BLANK (USPTO)

Title: Process for the production of crystalline energetic materials

The invention is directed to a process for the production of crystalline energetic materials having improved stability and sensitivity properties.

Examples of energetic materials are energetic
5 oxidisers and explosives. High energy oxidisers are used as component in solid propellants for launchers and related applications. Examples of such oxidisers are hydrazinium nitroformate (HNF), nitramine hexaazaisowurtzitane (CL-20),
10 ammonium dinitramide (ADN), ammonium-perchlorate (AP) and the like. Other materials falling in this class of energetic materials are explosives like cyclotrimethylene trinitramine (Hexogen, RDX), cyclotetramethylene tetranitramine (Octogen, HMX) and pentaerythrol tetranitrate (PETN).

15 These materials are all produced in a manner, wherein at some time during their preparation a crystallisation step occurs. Sometimes also a purifying recrystallisation step is included in the process. As the final product form of these materials is crystalline, one
20 of the final steps of such a process includes a crystallisation.

For these crystalline energetic materials stability and sensitivity are very important parameters. Stability is of course important, as it determines the possible shelf
25 life of the material during long term storage, and it further plays a role in the conditions under which the material can be stored and used (wider temperature range of storage and application conditions). More stable materials need less strict conditions for storage and use, or may be
30 stored for a longer period of time under the same conditions.

The sensitivity, and more in particular the friction sensitivity and the impact sensitivity, are important, as it determines the care that should be taken during handling

and transport of the material. Also sensitivity determines to a large extent the governmental restrictions posed on transport and storage.

It is accordingly one object of the present
5 invention to improve the stability of crystalline energetic materials. It is another object of the invention to improve the sensitivity, such as impact and friction sensitivity thereof.

These and other objects are realised by the present
10 invention, which comprises a process for the production of crystalline energetic materials having improved stability and/or decreased sensitivity by crystallisation of the energetic materials with ultrasonic vibration having a frequency of between 10 and 100 kHz. Preferably the
15 amplitude of an ultrasonic probe used for producing the vibration is between 0.4 and 10 μm .

The present invention is based on the surprising discovery, that by carrying out the last crystallisation step in the presence of ultrasonic vibration with a
20 frequency of between 10 and 100 kHz, the morphology, stability and sensitivity can be improved, i.e. the crystals become more rounded, the stability is better and the sensitivity is less.

In US patent No. 3,222,231 published on December 7,
25 1965, it is disclosed to improve the morphology of crystalline material, including ammonium perchlorate and hydrazinium nitroformate, by precipitating a solid solute out of solution, while mechanically agitating the solution and subjecting it to a high frequency vibration. According
30 to this patent, the processing under vibration improves the morphology of the crystals. The disclosure of this patent does not indicate anything about the effect of the treatment on stability and sensitivity.

According to a more preferred embodiment the present
35 invention is directed to an improvement in the production of hydrazinium nitroformate (HNF). HNF belongs to the class

of high energy oxidisers and can be used in high performance chlorine free solid propellants.

HNF is generally produced in crystalline form by combining hydrazine and nitroform under well defined conditions, followed by further purification using i.a. crystallisation. One method for the production of HNF is described in US patent number 5,557,015. According to this method HNF is prepared in very pure form by reacting hydrazine and nitroform in a system that is a solvent for nitroform and a non-solvent for hydrazinium nitroformate, in the presence of a proton transferring medium.

The stability of the present energetic materials, and more in particular of HNF, can be determined by vacuum thermal stability (VTS) in accordance with STANAG 4479 at 60 and 80°C for 48 to 100 hours.

The friction sensitivity is determined by BAM friction in accordance with ONU 3b)i), the impact sensitivity by BAM impact in accordance with ONU 3a)ii).

It has been noted that whereas the HNF crystals are having an aspect ratio of more than 4 after crystallisation without ultrasonic vibration, the crystals produced in accordance with the process of the present invention have an aspect ratio, which is sometimes lower than this, depending both on the applied amplitude of the ultrasonic probe and the recrystallisation method used. However, it has also been found that there is no direct link between the aspect ratio of the crystals on the one hand and the stability or sensitivity on the other hand.

The process of the present invention can be carried out in various ways. In general it is important that during crystallisation the crystallising mixture is subjected to treatment with the ultrasonic vibration. This process can be applied during crystallisation and during recrystallisation.

In case of batch processing one may subject the whole batch at the same time to an ultrasonic vibration. In

the alternative it can be done by stirring the crystallising mixture in such a way that the batch content moves through a region of ultrasonic vibration sufficiently frequently to obtain the effect. This can for example be
5 done by using an ultrasonic probe, whereby the stirring regime or the construction of the crystalliser is such that the suspension passes the vibration zone frequently. It is also possible to include the treatment in a recirculation loop of the crystalliser.

10 The temperature of the treatment is not critical, although it may have some effect on the actual stability, sensitivity and morphology. Temperatures between 0 and 100°C, preferably between 15 and 75°C can be used.

The present invention is now explained on the basis
15 of the production of crystalline HNF, although it will be clear to the skilled person that other materials may be produced using the same principles, wherein variation may be applied, if necessary to take into account the actual production methods of other materials, while maintaining
20 the basic principles of the invention.

In the operation of the present invention first HNF is prepared from hydrazine and nitroform, for example as disclosed in the cited US patent No. 5.557.015, The contents of which is incorporated herein by way of
25 reference. In general this means that nitroform having a purity of more than 98.5 %, dissolved in dichloroethane, and water (6 vol.%) are mixed. At 0°C an equimolar amount of hydrazine, purity 99.5%, is added and the mixture is stirred, while keeping the temperature between 0 and 5°C.
30 The crystalline HNF obtained thereby is then subjected, either in the reaction mixture, or after crystallisation and/or additional purification, to a final (re)crystallisation in the presence of the ultrasonic vibration.

35 The invention is now further explained on the basis of a number of examples.

EXAMPLE 1

Nitroform, dissolved in dichloroethane (23 wt.%
5 nitroform), and water (6 vol.%) are mixed. At 0°C an
equimolar amount of hydrazine, purity 99.5%, is added and
the mixture is stirred, while keeping the temperature
between 0 and 5°C. The crystalline HNF obtained thereby is
separated from the mother liquor and redissolved in
10 methanol.

The HNF solution in methanol is subsequently cooled
yielding HNF crystals. This experiment has been performed
in the absence of ultrasound (US) (reference, amplitude
0 μm) and under ultrasonic vibration with a frequency of 20
15 kHz and varying ultrasonic amplitude. Figures 1, 2, 3 and 4
show the properties of HNF crystals obtained in several
experiments in which the amplitude of ultrasonic vibration
is varied during cooling crystallisation.

Figure 1 shows the positive effect of ultrasound
20 (US) on the morphology of HNF, expressed as the Length over
Diameter (L/D) and average particle size (X_{SPH}).

Figure 2 shows the positive effect of ultrasound
(US) on the sensitivity of HNF, expressed in BAM impact and
BAM friction values ([N] and [N.m] respectively).

25 Figure 3 shows that ultrasound (US) has a positive
effect on the thermal stability of HNF at 60°C. The initial
gas evolution decreases in comparison to the reference
sample (no ultrasound (US) = amplitude of 0 μm) and the gas
evolution in time decreases as well when a low amplitude of
30 0.4 μm is applied.

Figure 4 gives an indication of the positive effect
of ultrasound (US) on thermal stability at 80°C. At 80°C
the effect becomes more apparent (on the larger gas
evolution scale) after -80 hrs. These four figures clearly
35 show the positive effect of ultrasound (US) during cooling
crystallisation on morphology, sensitivity and stability in

comparison to the reference HNF crystallised in absence of ultrasound (US).

EXAMPLE 2 (ultrasound (US) applied during drowning
5 out crystallisation of HNF)

HNF is prepared by the method described in example 1. The HNF in methanol solution is subsequently closed in a methylene chloride/methanol solution yielding HNF crystals.
10 This experiment has been performed in the absence of ultrasound (US) (reference, amplitude 0 μm) and under ultrasonic vibration with a frequency of 20 kHz and varying ultrasonic amplitude. Figures 5, 6 and 7 show the properties of HNF crystals obtained in several experiments in which
15 the amplitude of ultrasonic vibration is varied during drowning out crystallisation.

Figure 5 shows the negative effect of ultrasound (US) on morphology; L/D increases which implies that the HNF crystals are more needle shaped.

20 Figures 6 and 7 show VTS results at 60 and 80°C, respectively.

From figure 6 it can be clearly seen that ultrasound (US) application reduces initial gas evolution with a minimum initial gas evolution at a low to medium ultrasound
25 (US) amplitude (0.4-2 μm).

Figure 7 shows that at higher temperature (80°C) the application of ultrasound (US) not only reduces the initial gas evolution but also the overall gas evolution rate in time. These three figures clearly show that in spite of the
30 negative influence of ultrasound (US) during drowning-out crystallisation on morphology, ultrasound (US) has a positive influence on stability in comparison to the reference HNF crystallised in absence of ultrasound (US).

Claims

1. Process for the production of crystalline energetic materials having improved stability and/or decreased sensitivity by crystallisation of the energetic materials with ultrasonic vibration having a frequency of between 10 and 100 kHz.
5
2. Process according to claim 1, wherein the crystallising mixture is stirred during crystallisation.
3. Process according to claim 1 or 2, wherein the crystallising mixture is transported continuously through
10 the zone of ultrasonic vibration.
4. Process according to claims 1-3, wherein the temperature during recrystallisation is between 15 and 75°C.
5. Process according to claims 1-4, wherein the ultrasonic
15 vibration is generated using an ultrasonic probe, the amplitude thereof being between 0.4 and 10 μm .
6. Process according to claims 1-5, wherein the energetic materials are selected from the group of explosives and high energy oxidisers.
- 20 7. Process according to claim 6, wherein the said energetic materials are selected from the group consisting of hydrazinium nitroformate, Cl2O, ADN, AP, RDX, HMX and PETN.

THIS PAGE BLANK (USPTO)

ABSTRACT

The invention is directed to a process for the production of crystalline energetic materials having improved stability and/or decreased sensitivity by crystallisation of the energetic materials with ultrasonic vibration having a frequency of between 10 and 100 kHz.

THIS PAGE BLANK (USPTO)

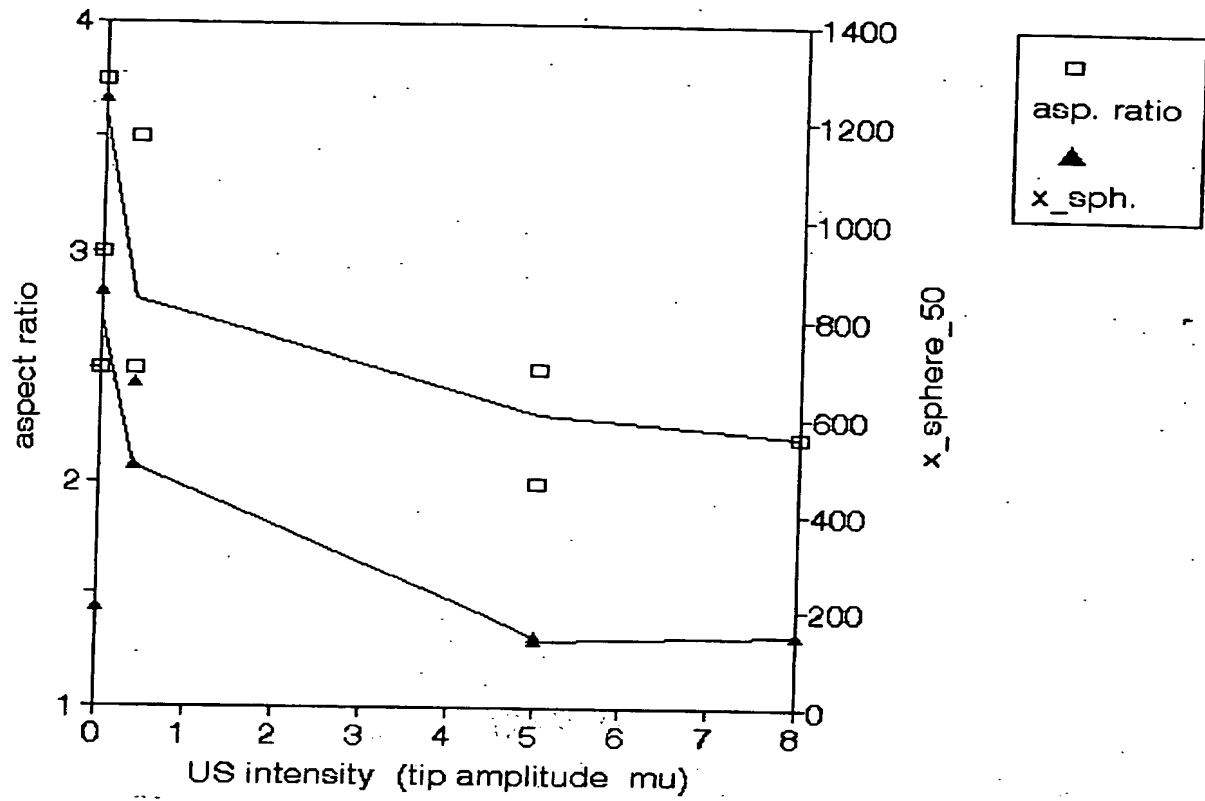


Figure 1

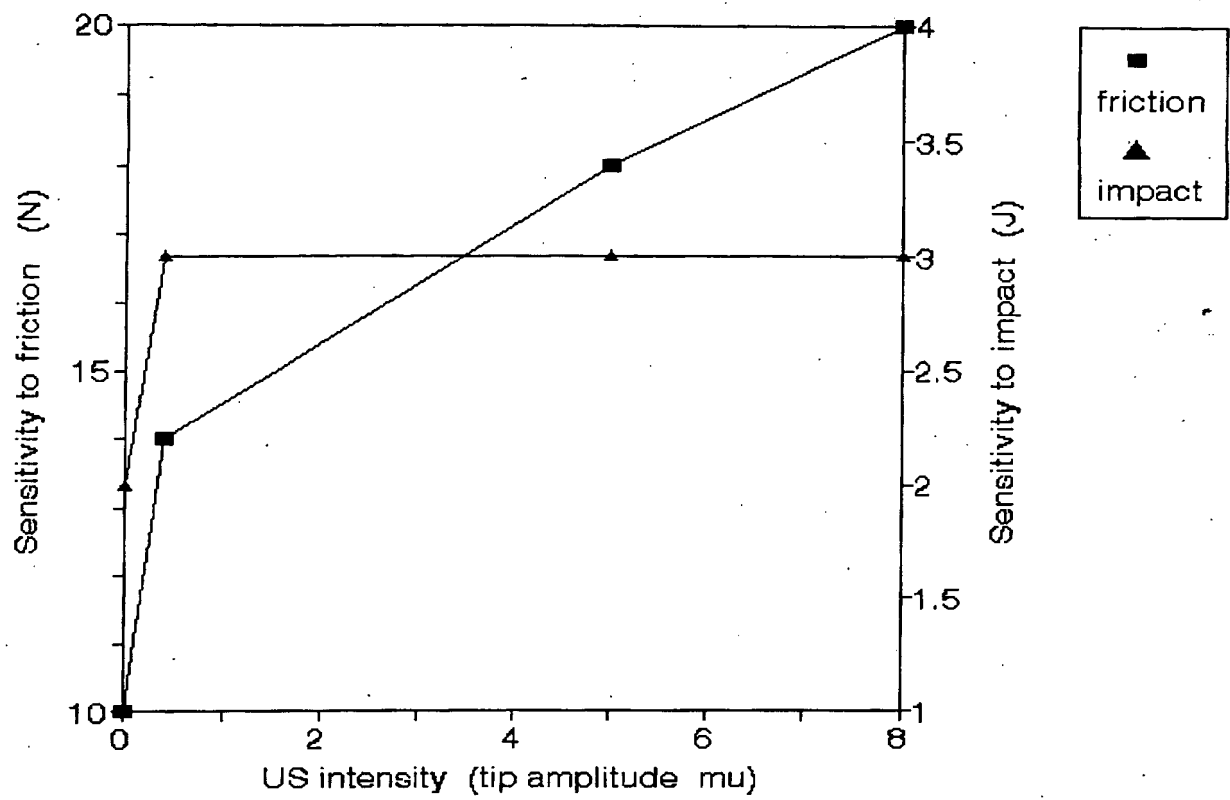


Figure 2

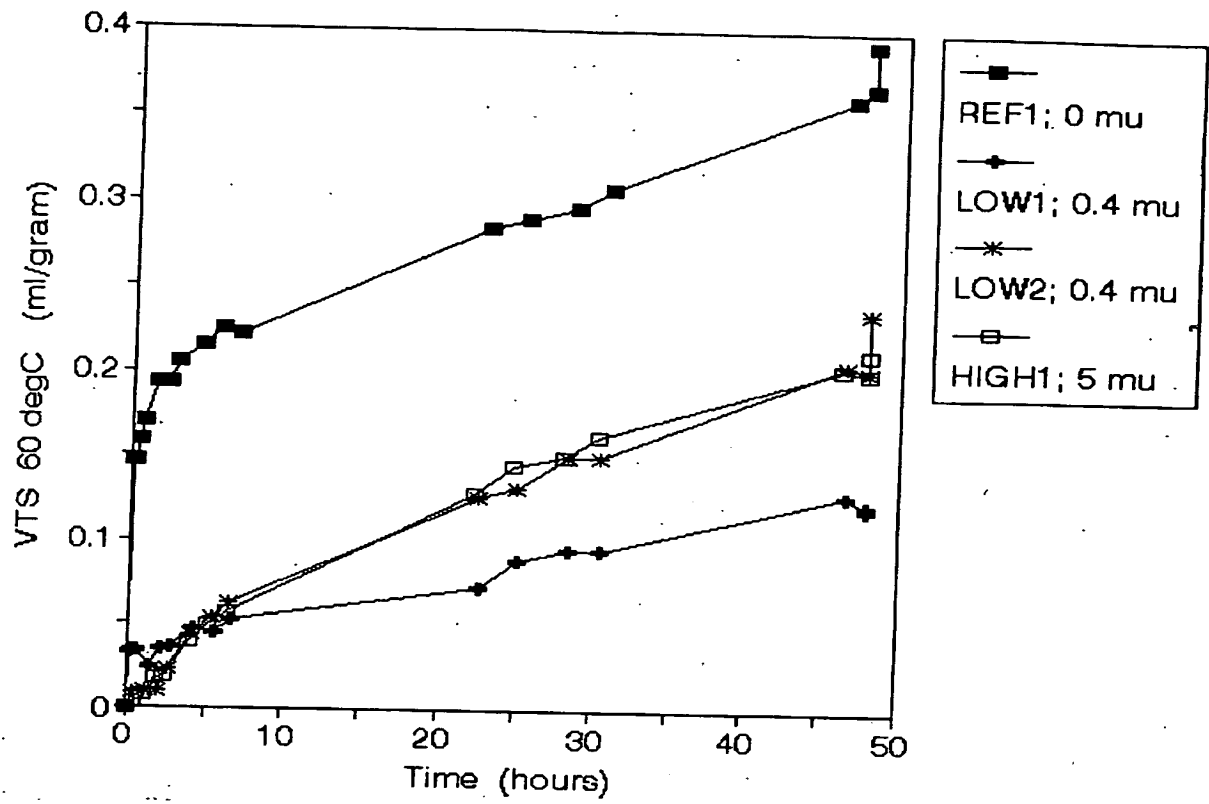


Figure 3

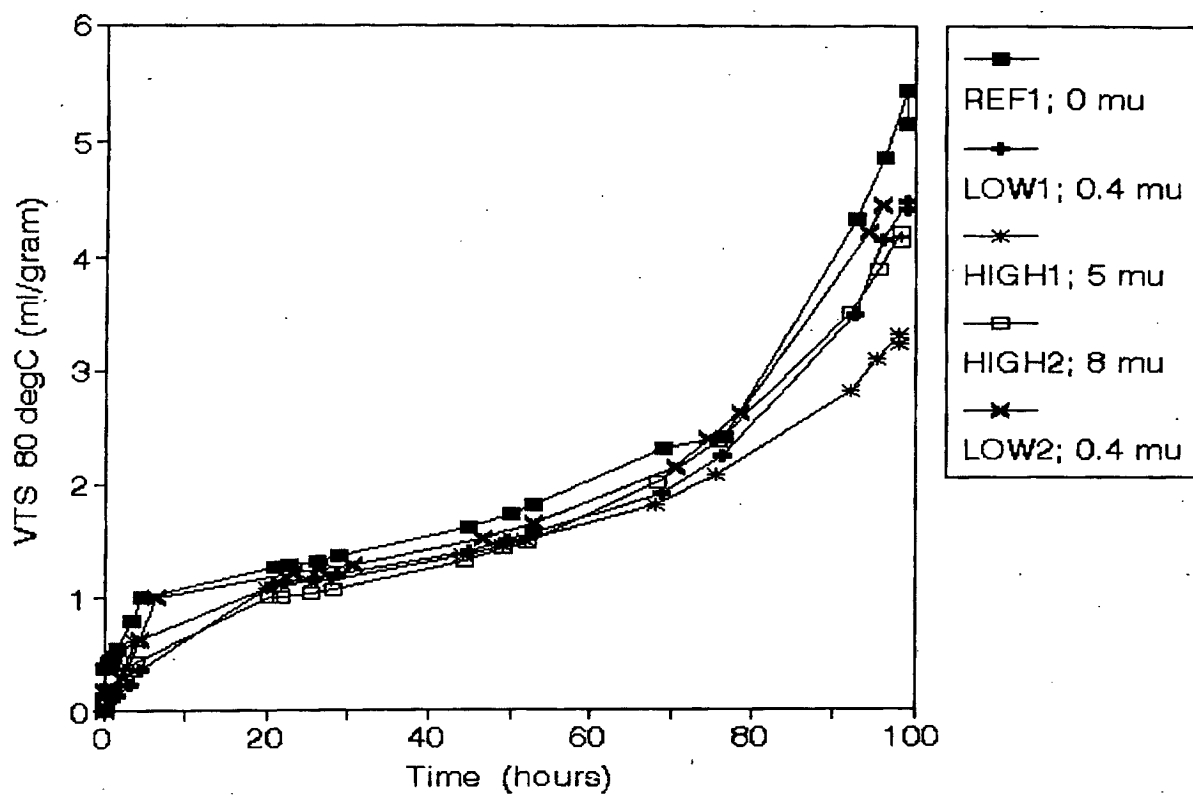


Figure 4

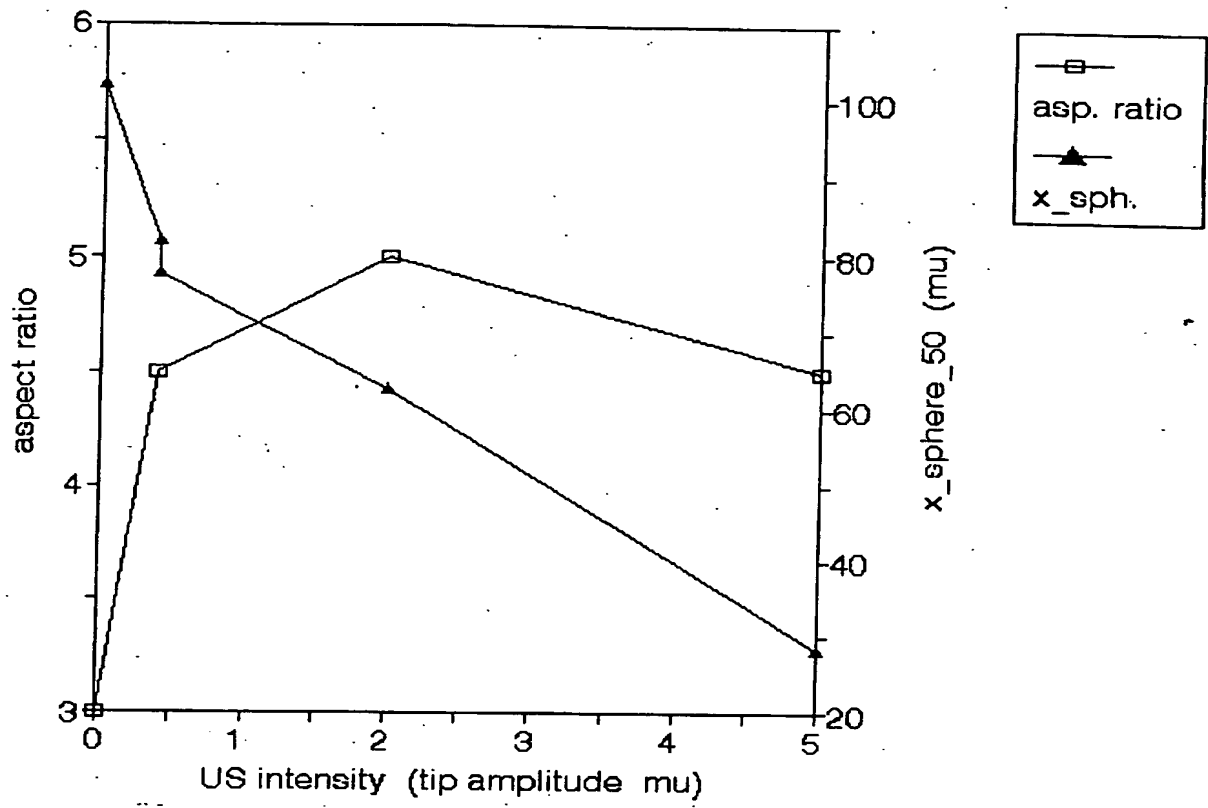


Figure 5

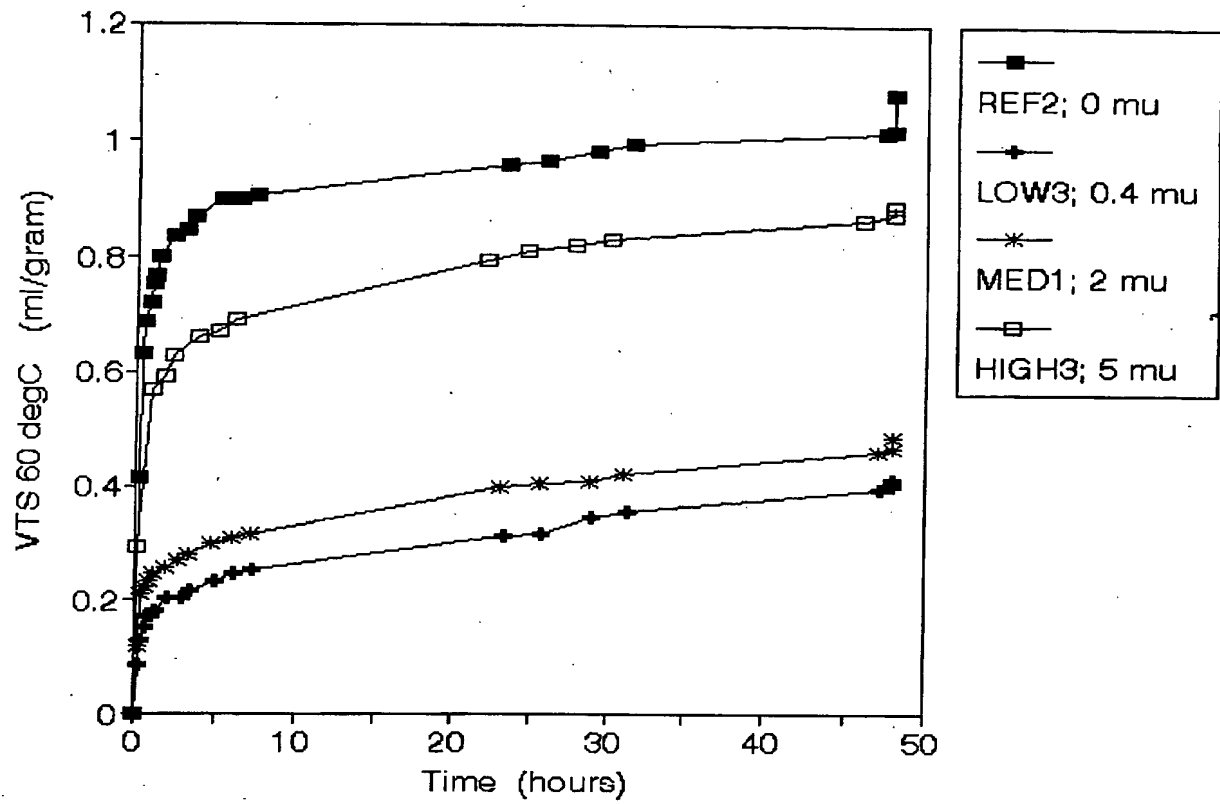


Figure 6

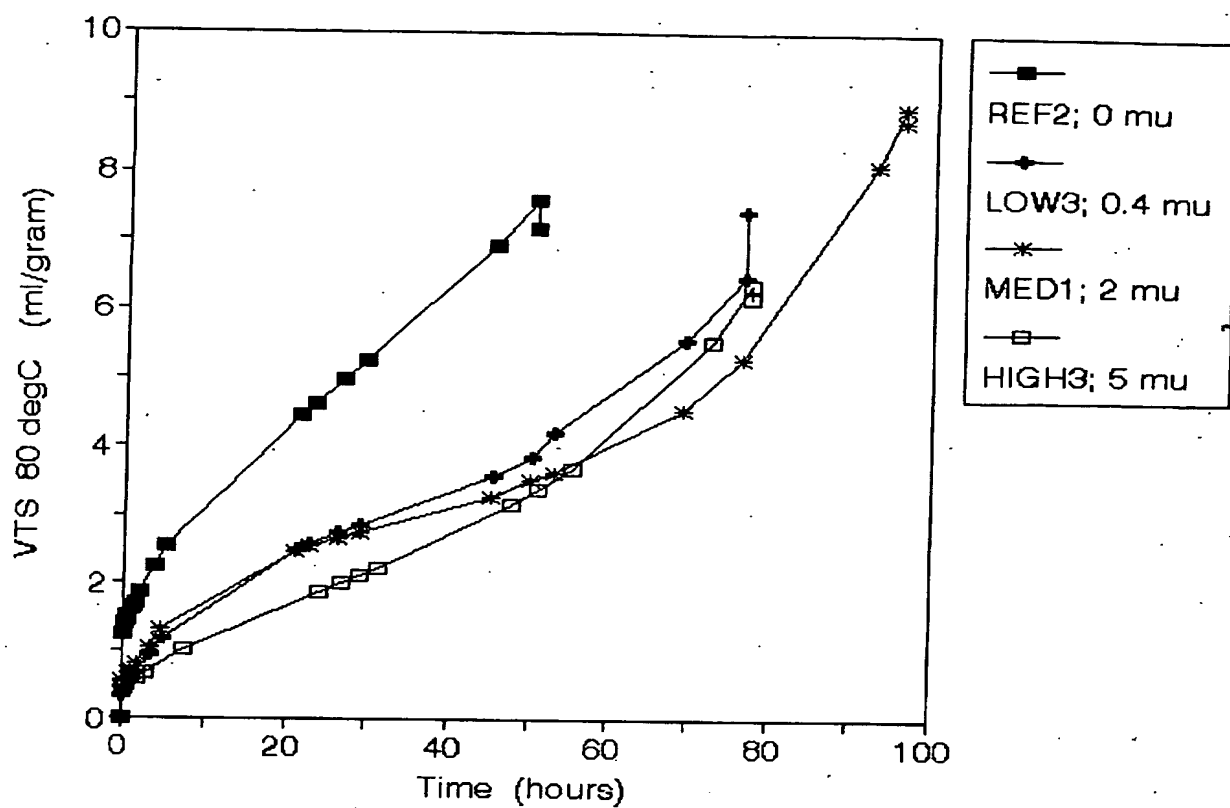


Figure 7

THIS PAGE BLANK (USPTO)